Urethane Foams From Animal Fats. VI. Improved Properties of Lard and Tallow-Based Foams[1]

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F. SCHOLNICK, E.J. SAGGESE, M. ZUBILLAGA, H.A. MONROE, JR., and A.N. WRIGLEY, Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania 19118

Abstract

Improved properties of fire retardant urethane foams prepared from hypobrominated lard and tallow have been obtained by purification of the polyols prior to their use. Hypobromination was carried out by epoxidation of the glycerides followed by treatment with gaseous HBr. The crude derivatives were extracted with acetone and separated from unreacted saturates at 5 C. One step hypochlorination of glycerides by use of acidified sodium hypochlorite has been carried out, and subsequent purification of the polyols led to minor foam property improvement. Fire retardant foams have also been prepared from soybean oil and monoolein using both of these general methods, although the acetone extraction step could be omitted.

Introduction

Previous work from this laboratory (1–5) has shown that rigid urethane foams can be prepared from polyols derived from animal fats. In our most recent communication (5) we described the preparation and evaluation of flame resistant foams using hypohalogenated glycerides as the polyol ingredient. Hypohalogenation was achieved either by treatment of epoxidized glycerides with HX or by direct addition of HOX to the unsaturated fatty substrate. At that time it was suggested that inferior foam properties such as lowered compressive strength and high percentage of open cells were caused by the presence of inert materials. It was believed that purification of the polyols would lead to subsequent improvement in properties.

We now report that removal of unreacted saturated materials from hypobrominated lard and tallow (prepared by addition of gaseous HBr to the epoxide) is achieved by cooling an acetone solution of the polyol. The saturates are precipitated at 5 C and easily separated. The purified polyols can be isolated by evaporation of the acetone and have been used in preparation of foams with improved properties. This method of purification was unnecessary for hypobrominated soybean oil or monoolein since these substrates contain lower amounts of saturates. In another modification of our previous work, direct addition of HOCl has been carried out more efficiently via acidified sodium hypochlorite rather than from calcium hypochlorite.

Experimental Procedures

Materials

The materials listed were used as received: Lard (Armour and Co.), iodine value 57.3 (found); tallow, fancy (Wilson-Martin Chemical Corp.), iodine value 51.3 (found); soybean oil (alkali bleached and refined), iodine value 136.7 (found); glyceryl monooleate (Eastman Organic Chemicals), iodine value 66.4 (found).

Procedures

Preparation of Hypohalogenated Glycerides from Epoxidized Glycerides: Epoxidized glycerides were obtained by treatment of lard, tallow, monoolein or soybean oil with peracetic acid using techniques previously described (6). Gaseous HBr was bubbled through the neat epoxides, in a flask equipped with a gas inlet tube, stirrer and thermometer. The temperature was maintained at 40–50 C in order to insure liquidity of the reaction mixture. With epoxidized soybean oil it was necessary to add chloroform to reduce viscosity. When no more HBr was absorbed as evidenced by the escape of hydrogen halide from the flask, the mixture was sparged with nitrogen to

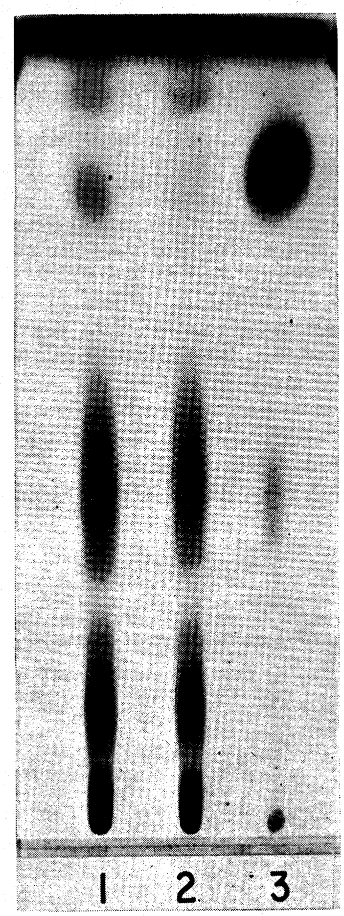

FIG. 1. 1, Crude hypobrominated tallow; 2, purified hypobrominated tallow; 3, saturates insoluble in acetone. System 95% benzene-5% ether.

[1] Presented at the AOCS Meeting, Chicago, September 1970.
[2] E. Market. Nutr. Res. Div., ARS, USDA.

TABLE I

Hypohalogenated Glycerides

Polyol	Per cent hydroxyl			Per cent halogen		
		Found			Found	
	Theory[a]	Crude	Purified	Theory[a]	Crude	Purified
Epoxidized lard + HBr	3.15	3.22	3.46	14.80	13.62	14.76
Epoxidized tallow + HBr	2.88	2.75	2.90	13.51	13.48	14.06
Epoxidized monoolean + HBr	11.15	8.67	.....	16.67	22.13	....
Epoxidized soybean oil + HBr	6.02	5.87	......	28.28	24.90	....
Lard + HOCl	3.43	1.22	2.12	7.15	13.33	14.56
Tallow + HOCl	3.11	1.18	1.50	6.48	10.82	11.31
Monoolein + HOCl	12.29	8.38	......	8.15	11.30	....
Soybean oil + HOCl	7.14	3.15	......	14.88	21.65	....

[a] Based upon original iodine value.

remove excess acid. The crude bromohydrins were analyzed for residual oxirane and unsaturation as well as for hydroxyl and halogen content.

Purification of hypobrominated lard and tallow was achieved by dissolving the crude material in 10 times its weight of acetone and chilling the solution to 5 C, filtering off the precipitated solid and evaporation of the filtrate under reduced pressure. The solid material consisted primarily of unreacted saturates and displayed no hydroxyl function. In a typical extraction of hypobrominated tallow, approximately 6.7% of the crude polyol was insoluble in the acetone. This method led to no precipitation when applied to hypobrominated monoolein or soybean oil, presumably because of the absence of appreciable quantities of saturated triglycerides. Analytical results, given in Table I, show that increases in hydroxyl and halogen content were attained by purification of hypobrominated lard and tallow. Figure 1 is a thin layer chromatogram of crude and purified hypobrominated tallow, and of the saturates removed by acetone extraction.

Direct Hypohalogenation: The general procedure used for direct hypochlorination is illustrated with tallow. One hundred grams of fancy tallow was suspended in 1 liter of water containing 0.5 g of an alkylbenzene sulfonate. To this was added 500 ml of 0.70 M sodium hypochlorite which had been adjusted to pH 4.7 with glacial acetic acid. The mixture was stirred at room temperature for 6 hr, the water layer removed by decantation and the residue extracted with several portions of chloroform. The extracts were washed with water until neutral, dried with magnesium sulfate and the solvent removed. The weight of crude polyol was 106.2 g.

Hypohalogenation products of lard and tallow were purified by the acetone extraction procedure described in the previous section. Once again hypohalogenated monoolein and soybean oil did not lend themselves to this method of purification. Analytical results are given in Table I. As previously noted (5), hypochlorination with HOCl is less effective than use of epoxidized glycerides; it results in lower hydroxyl content and formation of dihalide byproducts.

Foam Preparation and Test Methods. These were similar to methods described previously (5). The polyols were adjusted to an equivalent weight of 120 by addition of triisopropanolamine, and small (approximately 25 g) batches of foams were prepared and evaluated for density, per cent open cells, compressive strength and flammability characteristics. Results are summarized in Tables II and III.

Discussion

A comparison of properties of foams prepared from crude and purified hypobrominated lard and tallow (see Table II) reveals that the percentage of open cells in the final foam is decreased considerably when purified polyols are used. This lowering of open cell content is accompanied by increased compressive strength and improved fire resistance. Table II also indicates that foam properties comparable to those described above are obtained when crude polyols derived from hypobrominated soybean oil and monoolein are used. In most cases, addition of Sb_2O_3 improved the flammability rating but was accompanied by decreased compressive strength.

On the other hand, Table III shows that purification of hypochlorinated lard and tallow (obtained by the direct addition of HOCl) leads to no marked

TABLE II

Foams From Hypobrominated Glycerides (Epoxides + HBr)

Polyol source	Purity	Additive, 2%	Density, lb/ft^3	Open cells, %	Compressive strength, psi	Flammability rating[a]
Epoxidized lard + HBr	Crude	....	1.98	98.8	14.0	B
		Sb_2O_3	1.94	98.3	13.5	SE
	Purified	....	1.84	16.2	20.0	NB
		Sb_2O_3	1.94	16.2	20.0	NB
Epoxidized tallow + HBr		....	1.85	79.4	17.0	B
	Crude	Sb_2O_3	1.78	91.6	16.0	SE
		....	1.87	18.7	19.0	SE
	Purified	Sb_2O_3	1.88	18.0	17.0	NB
Epoxidized soybean oil + HBr		....	1.71	14.9	22.0	SE
	Crude	Sb_2O_3	1.70	15.6	18.0	NB
Epoxidized monoolein + HBr		....	1.84	16.5	23.0	NB
	Crude	Sb_2O_3	1.86	18.5	18.5	NB

[a] B, Burning; SE, self-extinguishing; NB, nonburning.

TABLE III

Foams From Hypochlorinated Glycerides (Direct Addition of HOCl)

Polyol source	Purity	Additive, 2%	Density, lb/ft^3	Open cells, %	Compressive strength, psi	Flam-ability rating[a]
Lard + HOCl	Crude	....	2.13	99.1	9.0	B
		Sb_2O_3	2.28	99.0	7.0	SE
	Purified	....	2.02	99.1	8.0	B
		Sb_2O_3	1.96	99.0	8.0	SE
Tallow + HOCl	Crude	....	2.26	97.8	5.0	B
		Sb_2O_3	2.53	97.0	7.0	B
	Purified	....	3.24	98.0	14.5	B
		Sb_2O_3	3.34	98.3	12.5	SE
Soybean oil + HOCl	Crude	....	1.68	29.2	15.0	B
		Sb_2O_3	1.66	36.9	15.0	NB
Monoolein + HOCl	Crude	....	1.85	16.6	25.0	B
		Sb_2O_3	1.78	17.7	19.0	NB

[a] B, Burning; SE, self-extinguishing; NB, nonburning.

lowering in per cent open cells, although some improvement in compressive strength and flammability rating is effected. Once more, foams prepared from crude hypochlorinated soybean oil and monoolein were comparable in properties to those obtained from purified lard and tallow hypochlorites.

In general, comparison of foam properties given in Tables II and III show that superior foams are obtained from hypohalogenated polyols prepared by reaction of HBr with epoxides rather than by direct HOCl addition. Apparently purer polyols are obtainable by the two-step synthesis, and this is borne out by the analytical data presented in Table I.

ACKNOWLEDGMENT

Halogen analyses by L.H. Scroggins of the Microanalytical Laboratory; cutting of foams by George Pisano of the Instrument Shop; sample of alkali refined and bleached soybean oil furnished by Northern Marketing and Nutrition Research Division, ARS, USDA.

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